METAL-ELEMENT COMPOUNDS OF TITANIUM, ZIRCONIUM, AND HAFNIUM AS PYROTECHNIC FUELS

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ABSTRACT

Conventional high-energy pyrotechnic fuels are typically metals, metalloids, or alloys. The use of inorganic compounds including ceramic materials in this role has been far less common. Following the development of boron carbide-based pyrotechnics in our laboratories, we have started to explore the pyrotechnic properties of other inorganic compounds, particularly those of titanium, zirconium, and hafnium. The transition metals of group 4 are well known as potent pyrotechnic fuels. However, metal powders are susceptible to aging and pyrotechnic compositions containing them can be sensitive to unintended ignition by electrostatic discharge. The use of the corresponding metal-element compounds may ameliorate these problems. Commercially available group 4 compounds containing hydrogen, boron, carbon, nitrogen, silicon, and phosphorus were obtained for an initial survey. The as-received materials were characterized by XRD, XRF, and SEM. Binary compositions containing these fuels and KNO_3 or Bi_2O_3 were prepared and tested. The experimental results were compared with the output from FactSage thermochemical software. Diverse observed and predicted behavior suggests that these compounds may be useful for a variety of pyrotechnic applications.

1. INTRODUCTION

The recent use of boron carbide in smoke, delay, and illuminant compositions clearly demonstrates the potential of ceramic materials as advanced pyrotechnic fuels [1-3]. As a natural extension of this work, we have since started to explore the pyrotechnic properties of metal-element compounds containing group 4 metals. The group 4 metals—titanium, zirconium, and hafnium—are potent pyrotechnic fuels. However, the metals themselves are often pyrophoric as fine powders [4,5] and pyrotechnic compositions containing them can be extremely sensitive to unintended ignition from electrostatic discharge [6]. Non-oxide group 4 ceramics (borides, carbides, nitrides, silicides) and related covalent network solids (hydrides, phosphides) allow access to the group 4 elements indirectly. Many of these materials are available commercially as fine powders. The purpose of this initial investigation was to survey their characteristics and reactivity with two common pyrotechnic oxidizers, KNO_3 and Bi_2O_3.

2. EXPERIMENTAL SECTION

2.1. Materials

Potassium nitrate (MIL-P-156B, hammer milled, approximately 15 μm) was obtained from Hummel Croton and contained 0.2 wt% fumed silica, Cabot CAB-O-SIL M-5, as an anticaking agent. Bismuth oxide (Bi_2O_3, approximately 10 μm) was obtained from Alfa Aesar. Group 4 metal-element compounds were obtained from Atlantic Equipment Engineers (AEE), Alfa Aesar, and American Elements. These were characterized by X-ray diffraction (XRD), X-ray fluorescence (XRF), and scanning electron microscopy (SEM).

2.2. Material Analyses

XRD was carried out in a Rigaku Ultima III diffractometer with CuKα radiation (1.54 Å). A step size of 0.02 degrees and a scan rate of 0.25 deg/min were used. The patterns were analyzed with JADE 7 software (Materials Data Inc., Livermore CA).

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14. ABSTRACT

Conventional high-energy pyrotechnic fuels are typically metals, metalloids, or alloys. The use of inorganic compounds including ceramic materials in this role has been far less common. Following the development of boron carbide-based pyrotechnics in our laboratories, we have started to explore the pyrotechnic properties of other inorganic compounds, particularly those of titanium, zirconium, and hafnium. The transition metals of group 4 are well known as potent pyrotechnic fuels. However, metal powders are susceptible to aging and pyrotechnic compositions containing them can be sensitive to unintended ignition by electrostatic discharge. The use of the corresponding metal-element compounds may ameliorate these problems. Commercially available group 4 compounds containing hydrogen, boron, carbon, nitrogen, silicon, and phosphorus were obtained for an initial survey. The as-received materials were characterized by XRD, XRF, and SEM. Binary compositions containing these fuels and KNO3 or Bi2O3 were prepared and tested. The experimental results were compared with the output from FactSage thermochemical software. Diverse observed and predicted behavior suggests that these compounds may be useful for a variety of pyrotechnic applications.

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Semi-quantitative chemical composition analysis was carried out in a Rigaku ZSX Primus II wavelength dispersive XRF spectrometer. The spectrometer contained a 4 kW Rh anode and the detector system used a scintillation counter for detecting heavy elements and a flow proportional counter for detecting light elements. The samples were tested in a vacuum and the data were analyzed using SQX software that can correct for matrix effects, overlapping lines, and secondary excitation effects by photoelectrons. Increased accuracy was achieved using built-in matching library and perfect scan analysis programs.

SEM was performed with a Zeiss Supra 40VP variable pressure field emission scanning electron microscope. Superb resolution and image quality at low operating voltages allows examination of non-conducting samples without any conductive coating.

2.3. Experimental Methods

Binary mixtures of the fuels and KNO_3 or Bi_2O_3 were prepared by combining the components in small conductive containers and mixing with a Scientific Industries Vortex Genie vibrating shaker. Each composition was mixed for 3 min. Two grams of each mixture was placed in an unconsolidated pile on a steel cylinder. The point of a nichrome wire was placed in the center of each pile. For each test, a digital video recording was used to capture the resulting qualitative behavior as the nichrome wire was electrically heated.

2.4. Computational Methods

Thermodynamic calculations were performed with FactSage 6.4 (Thermfact/CRCT and GTT-Technologies). The particular calculations presented in this paper made use of the FactPS and FToxid databases. The analyses were conducted in adiabatic mode ($\Delta H = 0$). The results consist of predicted adiabatic reaction temperatures and the thermodynamic products at those temperatures.

3. RESULTS

The results of the experimental ignition tests must be evaluated in the context of the material properties (Table 1). XRD was used to determine phase purity or to detect the presence of other phases. With only two exceptions, the compounds were phase pure or nearly so, containing small amounts of crystalline impurities. Titanium phosphide, sold as TiP, contained a substantial amount of Ti_5P_3. Zirconium silicide ($ZrSi_2$) contained a large amount of Si, along with $ZrSiO_4$ and ZrO_2.

Elemental compositions were determined semi-quantitatively by XRF. Common elemental impurities included Fe and Cr. In some cases, these may have been introduced through milling by the manufacturer. The zirconium compounds contained small amounts of Ti and/or Hf. The hafnium compounds all contained small amounts of Zr. Importantly, these impurities were not necessarily present as elemental materials and were most likely contained within compounds that were not detected by XRD or were not crystalline.

SEM was used to assess approximate particle size and qualitative sample characteristics. Many of the materials appeared to have been milled, as evidenced by sharp jagged edges and numerous fines. Some (ZrC, HfB_2, HfC) were clearly present as they had crystallized and did not appear to have been milled to any significant degree. Others (TiB_2, TiC) appeared to have been milled for a short time. Several examples are presented in Figures 1a-d.

Balanced stoichiometries for simple binary combustion reactions may be calculated if certain products are assumed. Tables 2a-d show the results for such assumed reactions. In these tables, the group 4 metals are assumed to form the corresponding dioxides. Other elements are assumed to form simple oxides. Nitrogen from the nitrides and KNO_3 is assumed to form N_2, while the bismuth in Bi_2O_3 is assumed to form elemental Bi.

For each binary system, FactSage was used to determine the stoichiometry with the highest predicted adiabatic temperature (T_{ad}). This was accomplished by scanning each combination in 1 wt% intervals. Tables 3a-d show the peak T_{ad} values, the corresponding stoichiometries, and the major predicted products (at the adiabatic temperatures). Some compounds (Ti_5Si_3, TiP, $HfSi_2$) were not in the FactSage databases, so systems containing them could not be modeled.

Tables 4a-d show the results of experimental ignition tests. In these experiments, the stoichiometries obtained from FactSage (Tables 3a-d) were used where available. For combinations containing Ti_5Si_3, TiP, and $HfSi_2$, the stoichiometries from Tables 2a-d were used.

Table 1. Material Properties

Compound	Vendor	XRD Analysis	XRF Impurities (0.1-2 wt%)	SEM Particle Size (μm)	SEM Apparent Characteristics
TiH_2	Alfa Aesar	phase pure ($TiH_{1.95}$)	-	fines < 2 intermediate 2-8	milled
TiB_2	AEE	phase pure	-	mostly 1-7	minimally processed
TiC	Alfa Aesar	phase pure ($TiC_{0.93}$)	Fe, Cr, V	fines < 1 intermediate 2-8	minimally processed
TiN	AEE	phase pure	Fe	fines < 1 intermediate 2-8	milled
$TiSi_2$	AEE	trace TiSi, trace SiO_2	Fe, Cr, Al	fines < 2 int. 5-20, coarse 50-100	milled
Ti_5Si_3	Alfa Aesar	phase pure	Fe, Cr	fines < 2 int. 5-10, coarse 20-40	milled
TiP	American Elements	TiP, Ti_5P_3	Si, Al, Fe	fines < 2 intermediate 5-15	milled
ZrB_2	AEE	phase pure	Ti, Fe, Ca	fines < 2 intermediate 5-20	milled
ZrC	AEE	phase pure	Fe, Ti, Cr	fines < 3 intermediate 10-30	as crystallized
ZrN	AEE	trace Zr_3O	Hf, Ti, Fe, Er, Cr	fines < 1 intermediate 5-25	milled
$ZrSi_2$	AEE	Si, $ZrSi_2$, $ZrSiO_4$, ZrO_2	Ti, Hf, Fe, Al, Cr	fines < 1 int. 2-10, coarse 30-60	milled
HfB_2	AEE	phase pure	Zr	fines 1-2 intermediate 5-10	as crystallized
HfC	AEE	phase pure	Zr	< 3	as crystallized
$HfSi_2$	AEE	trace HfO_2	Fe, Zr, Cr	fines < 1 intermediate 2-25	milled

Table 2a. Estimated Combustion Stoichiometry – Titanium Compounds, KNO_3

Equation	Fuel (wt%)	Oxidizer (wt%)
$5\ TiH_2 + 6\ KNO_3 \rightarrow 5\ TiO_2 + 5\ H_2O + 3\ K_2O + 3\ N_2$	29	71
$TiB_2 + 2\ KNO_3 \rightarrow TiO_2 + B_2O_3 + K_2O + N_2$	26	74
$5\ TiC + 8\ KNO_3 \rightarrow 5\ TiO_2 + 5\ CO_2 + 4\ K_2O + 4\ N_2$	27	73
$10\ TiN + 8\ KNO_3 \rightarrow 10\ TiO_2 + 9\ N_2 + 4\ K_2O$	43	57
$5\ TiSi_2 + 12\ KNO_3 \rightarrow 5\ TiO_2 + 10\ SiO_2 + 6\ K_2O + 6\ N_2$	30	70
$5\ Ti_5Si_3 + 32\ KNO_3 \rightarrow 25\ TiO_2 + 15\ SiO_2 + 16\ K_2O + 16\ N_2$	33	67
$10\ TiP + 18\ KNO_3 \rightarrow 10\ TiO_2 + 5\ P_2O_5 + 9\ K_2O + 9\ N_2$	30	70

Table 3a. FactSage Calculations – Titanium Compounds, KNO_3

Reactant Fuel	T_{ad} (°C)	Fuel / KNO_3 (wt% ratio)	Major Products (*phase*, wt%)
TiH_2	2495	41 / 59	Ti_3O_5 (*s*, 59.9), K (*g*, 19.9), N_2 (*g*, 8.2), H_2O (*g*, 5.2), KOH (*g*, 4.0)
TiB_2	2868	26 / 74	TiO_2 (*l*, 16.3), Ti_2O_3 (*l*, 8.7), KBO_2 (*g*, 56.0), N_2 (*g*, 10.1), TiO_2 (*g*, 3.5)
TiC	2185	30 / 70	$K_2Ti_6O_{13}$ (*s*, 40.6), TiO_2 (*l*, 6.0), K (*g*, 21.1), CO_2 (*g*, 18.5), N_2 (*g*, 9.6), CO (*g*, 2.3)
TiN	2176	45 / 55	$K_2Ti_6O_{13}$ (*s*, 60.8), TiO_2 (*l*, 7.3), N_2 (*g*, 17.7), K (*g*, 12.7)
$TiSi_2$	2733	33 / 67	$K_2Si_4O_9$ (*l*, 30.6), TiO_2 (*l*, 23.9), K (*g*, 18.2), SiO (*g*, 10.4), N_2 (*g*, 9.0), O_2 (*g*, 2.6)
Ti_5Si_3	-	-	-
TiP	-	-	-

Table 4a. Experimental Results – Titanium Compounds, KNO_3

(*a*) Mixture (*b*) wt% Ratio	Ignition	Self-Sustained Combustion	Amount Consumed	(*a*) Type (*b*) Duration (s)	Flame	(*a*) Sparks (*b*) Smoke (*c*) Slag
(*a*) TiH_2 / KNO_3 (*b*) 41 / 59	yes	yes	all	(*a*) flash (*b*) 0.3	large, white with violet tinge	(*a*) some, white-yellow (*b*) obscured by flash (*c*) none
(*a*) TiB_2 / KNO_3 (*b*) 26 / 74	yes	yes	part	(*a*) sparkler (*b*) 6	small, white with green tinge	(*a*) lots, yellow (*b*) white (*c*) some
(*a*) TiC / KNO_3 (*b*) 30 / 70	yes	no	part	(*a*) sparkler (*b*) 2	small, white with violet tinge	(*a*) lots, yellow (*b*) some, white (*c*) some
(*a*) TiN / KNO_3 (*b*) 45 / 55	no	no	part heated	(*a*) N/A (*b*) N/A	N/A	(*a*) N/A (*b*) fumes on heating (*c*) some, where heated
(*a*) $TiSi_2$ / KNO_3 (*b*) 33 / 67	yes	yes	part	(*a*) incandescent slag pile (*b*) 5	none	(*a*) none (*b*) some, white (*c*) lots
(*a*) Ti_5Si_3 / KNO_3 (*b*) 33 / 67	yes	yes	all	(*a*) sparkler (*b*) 2	small, white	(*a*) lots, white-yellow (*b*) white (*c*) some
(*a*) TiP / KNO_3 (*b*) 30 / 70	yes	no	part	(*a*) intermittent flash/spark (*b*) N/A	small, white	(*a*) some, white (*b*) white (*c*) some

Table 2b. Estimated Combustion Stoichiometry – Zirconium and Hafnium Compounds, KNO_3

Equation	Fuel (wt%)	Oxidizer (wt%)
$ZrB_2 + 2\ KNO_3 \rightarrow ZrO_2 + B_2O_3 + K_2O + N_2$	36	64
$5\ ZrC + 8\ KNO_3 \rightarrow 5\ ZrO_2 + 5\ CO_2 + 4\ K_2O + 4\ N_2$	39	61
$10\ ZrN + 8\ KNO_3 \rightarrow 10\ ZrO_2 + 9\ N_2 + 4\ K_2O$	57	43
$5\ ZrSi_2 + 12\ KNO_3 \rightarrow 5\ ZrO_2 + 10\ SiO_2 + 6\ K_2O + 6\ N_2$	38	62
$HfB_2 + 2\ KNO_3 \rightarrow HfO_2 + B_2O_3 + K_2O + N_2$	50	50
$5\ HfC + 8\ KNO_3 \rightarrow 5\ HfO_2 + 5\ CO_2 + 4\ K_2O + 4\ N_2$	54	46
$5\ HfSi_2 + 12\ KNO_3 \rightarrow 5\ HfO_2 + 10\ SiO_2 + 6\ K_2O + 6\ N_2$	49	51

Table 3b. FactSage Calculations – Zirconium and Hafnium Compounds, KNO_3

Reactant Fuel	T_{ad} (°C)	Fuel / KNO_3 (wt% ratio)	Major Products (*phase*, wt%)
ZrB_2	3099	36 / 64	ZrO_2 (*l*, 38.9), KBO_2 (*g*, 43.8), N_2 (*g*, 8.8), K (*g*, 3.8)
ZrC	2678	49 / 51	ZrO_2 (*s*, 51.8), ZrO_2 (*l*, 6.7), K (*g*, 19.6), CO (*g*, 11.3), N_2 (*g*, 7.0), CO_2 (*g*, 3.2)
ZrN	2678	61 / 39	ZrO_2 (*s*, 57.1), ZrO_2 (*l*, 14.1), K (*g*, 15.1), N_2 (*g*, 13.5)
$ZrSi_2$	2754	41 / 59	ZrO_2 (*l*, 34.3), $K_2Si_4O_9$ (*l*, 23.8), K (*g*, 16.7), SiO (*g*, 11.2), N_2 (*g*, 7.9), O_2 (*g*, 3.0)
HfB_2	3074	50 / 50	HfO_2 (*l*, 52.6), KBO_2 (*g*, 34.6), N_2 (*g*, 6.8), K (*g*, 2.8)
HfC	2557	65 / 35	HfO_2 (*s*, 71.8), K (*g*, 13.5), CO (*g*, 9.2), N_2 (*g*, 4.8)
$HfSi_2$	-	-	-

Table 4b. Experimental Results – Zirconium and Hafnium Compounds, KNO_3

(*a*) Mixture (*b*) wt% Ratio	Ignition	Self-Sustained Combustion	Amount Consumed	(*a*) Type (*b*) Duration (s)	Flame	(*a*) Sparks (*b*) Smoke (*c*) Slag
(*a*) ZrB_2 / KNO_3 (*b*) 36 / 64	yes	yes	part	(*a*) pulsating flash/flame (*b*) 4	moderate, green	(*a*) none (*b*) white (*c*) moderate
(*a*) ZrC / KNO_3 (*b*) 49 / 51	yes	yes	all	(*a*) flame (*b*) 1.7	moderate, white with violet tinge	(*a*) minimal, yellow (*b*) white (*c*) crusty white slag
(*a*) ZrN / KNO_3 (*b*) 61 / 39	yes	yes	all	(*a*) flame (*b*) 1.3	moderate, yellow	(*a*) some, yellow (*b*) white (*c*) crusty white slag
(*a*) $ZrSi_2$ / KNO_3 (*b*) 41 / 59	no	no	part heated	(*a*) N/A (*b*) N/A	N/A	(*a*) N/A (*b*) fumes on heating (*c*) some, where heated
(*a*) HfB_2 / KNO_3 (*b*) 50 / 50	yes	yes	all	(*a*) flame (*b*) 1.6	large, green	(*a*) on ignition, white (*b*) white (*c*) almost none
(*a*) HfC / KNO_3 (*b*) 65 / 35	yes	yes	all	(*a*) photoflash (*b*) < 0.1	large, white with violet tinge	(*a*) some, yellow (*b*) obscured by flash (*c*) none
(*a*) $HfSi_2$ / KNO_3 (*b*) 49 / 51	yes	yes	all	(*a*) sparkler (*b*) 5	small, white	(*a*) lots, white (*b*) white (*c*) lots

Table 2c. Estimated Combustion Stoichiometry – Titanium Compounds, Bi_2O_3

Equation	Fuel (wt%)	Oxidizer (wt%)
$TiH_2 + Bi_2O_3 \rightarrow TiO_2 + H_2O + 2\ Bi$	10	90
$3\ TiB_2 + 5\ Bi_2O_3 \rightarrow 3\ TiO_2 + 3\ B_2O_3 + 10\ Bi$	8	92
$3\ TiC + 4\ Bi_2O_3 \rightarrow 3\ TiO_2 + 3\ CO_2 + 8\ Bi$	9	91
$6\ TiN + 4\ Bi_2O_3 \rightarrow 6\ TiO_2 + 3\ N_2 + 8\ Bi$	17	83
$TiSi_2 + 2\ Bi_2O_3 \rightarrow TiO_2 + 2\ SiO_2 + 4\ Bi$	10	90
$3\ Ti_5Si_3 + 16\ Bi_2O_3 \rightarrow 15\ TiO_2 + 9\ SiO_2 + 32\ Bi$	12	88
$2\ TiP + 3\ Bi_2O_3 \rightarrow 2\ TiO_2 + P_2O_5 + 6\ Bi$	10	90

Table 3c. FactSage Calculations – Titanium Compounds, Bi_2O_3

Reactant Fuel	T_{ad} (°C)	Fuel / Bi_2O_3 (wt% ratio)	Major Products (*phase*, wt%)
TiH_2	1531	14 / 86	Ti_7O_{13} (*s*, 19.0), Ti_8O_{15} (*s*, 2.8), Bi_2 (*g*, 44.7), Bi (*g*, 32.5)
TiB_2	1618	9 / 91	Ti_3O_5 (*s*, 9.4), B_2O_3 (*l*, 8.4), Bi_2 (*g*, 48.3), Bi (*g*, 33.4)
TiC	1402	9 / 91	TiO_2 (*s*, 12.0), Bi (*l*, 60.7), Bi_2 (*g*, 14.1), Bi (*g*, 6.8), CO_2 (*g*, 5.9)
TiN	1375	17 / 83	$Ti_{20}O_{39}$ (*s*, 19.5), $Ti_{10}O_{19}$ (*s*, 2.2), Bi (*l*, 60.1), Bi_2 (*g*, 9.8), Bi (*g*, 4.6), N_2 (*g*, 3.8)
$TiSi_2$	1994	10 / 90	SiO_2 (*l*, 11.5), TiO_2 (*l*, 7.7), Bi (*g*, 64.3), Bi_2 (*g*, 15.8)
Ti_5Si_3	-	-	-
TiP	-	-	-

Table 4c. Experimental Results – Titanium Compounds, Bi_2O_3

(*a*) Mixture (*b*) wt% Ratio	Ignition	Self-Sustained Combustion	Amount Consumed	(*a*) Type (*b*) Duration (s)	Flame	(*a*) Sparks (*b*) Smoke (*c*) Slag
(*a*) TiH_2 / Bi_2O_3 (*b*) 14 / 86	yes	yes	all	(*a*) burst (*b*) 0.2	large, yellow-orange	(*a*) white, branching (*b*) lots, yellow (*c*) none
(*a*) TiB_2 / Bi_2O_3 (*b*) 9 / 91	yes	yes	all	(*a*) burst (*b*) 0.2	large, yellow-orange	(*a*) none (*b*) lots, yellow (*c*) almost none
(*a*) TiC / Bi_2O_3 (*b*) 9 / 91	difficult	no	part heated	(*a*) N/A (*b*) N/A	small, orange, where heated	(*a*) none (*b*) some, yellow (*c*) some, where heated
(*a*) TiN / Bi_2O_3 (*b*) 17 / 83	yes	yes	all	(*a*) slow-burning (*b*) 6	small, orange	(*a*) none (*b*) minimal, yellow (*c*) lots
(*a*) $TiSi_2$ / Bi_2O_3 (*b*) 10 / 90	yes	yes	all	(*a*) incandescent slag pile (*b*) 5	very small, orange	(*a*) none (*b*) minimal, yellow (*c*) lots
(*a*) Ti_5Si_3 / Bi_2O_3 (*b*) 12 / 88	yes	yes	all	(*a*) flame (*b*) 0.6	moderate, orange	(*a*) some, white (*b*) lots, yellow (*c*) metallic beads
(*a*) TiP / Bi_2O_3 (*b*) 10 / 90	yes	yes	all	(*a*) burst (*b*) 0.2	large, yellow-orange	(*a*) none (*b*) lots, yellow (*c*) none

Table 2d. Estimated Combustion Stoichiometry – Zirconium and Hafnium Compounds, Bi_2O_3

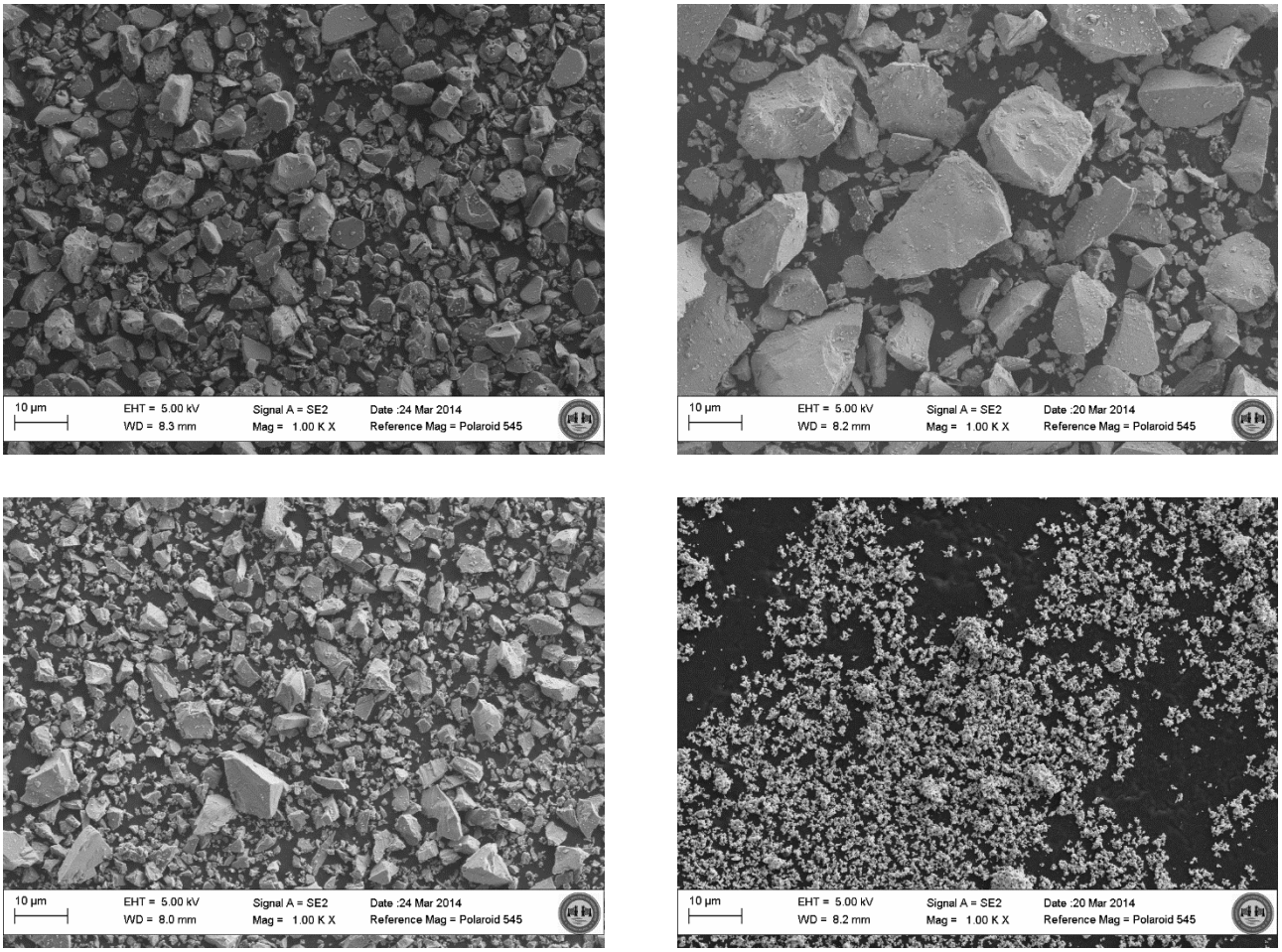
Equation	Fuel (wt%)	Oxidizer (wt%)
$3\ ZrB_2 + 5\ Bi_2O_3 \rightarrow 3\ ZrO_2 + 3\ B_2O_3 + 10\ Bi$	13	87
$3\ ZrC + 4\ Bi_2O_3 \rightarrow 3\ ZrO_2 + 3\ CO_2 + 8\ Bi$	14	86
$6\ ZrN + 4\ Bi_2O_3 \rightarrow 6\ ZrO_2 + 3\ N_2 + 8\ Bi$	25	75
$ZrSi_2 + 2\ Bi_2O_3 \rightarrow ZrO_2 + 2\ SiO_2 + 4\ Bi$	14	86
$3\ HfB_2 + 5\ Bi_2O_3 \rightarrow 3\ HfO_2 + 3\ B_2O_3 + 10\ Bi$	20	80
$3\ HfC + 4\ Bi_2O_3 \rightarrow 3\ HfO_2 + 3\ CO_2 + 8\ Bi$	23	77
$HfSi_2 + 2\ Bi_2O_3 \rightarrow HfO_2 + 2\ SiO_2 + 4\ Bi$	20	80

Table 3d. FactSage Calculations – Zirconium and Hafnium Compounds, Bi_2O_3

Reactant Fuel	T_{ad} (°C)	Fuel / Bi_2O_3 (wt% ratio)	Major Products (*phase*, wt%)
ZrB_2	1711	13 / 87	ZrO_2 (*s*, 14.0), B_2O_3 (*l*, 6.5), Bi (*g*, 41.4), Bi_2 (*g*, 36.6)
ZrC	1554	21 / 79	ZrO_2 (*s*, 24.4), Bi_2 (*g*, 43.1), Bi (*g*, 27.8), CO (*g*, 3.1)
ZrN	1494	26 / 74	ZrO_2 (*s*, 29.4), Bi (*l*, 9.8), Bi_2 (*g*, 37.4), Bi (*g*, 19.1), N_2 (*g*, 3.3)
$ZrSi_2$	2266	14 / 86	ZrO_2 (*s*, 11.7), SiO_2 (*l*, 10.4), Bi (*g*, 71.4), Bi_2 (*g*, 5.5)
HfB_2	1712	20 / 80	HfO_2 (*s*, 21.0), B_2O_3 (*l*, 6.2), Bi (*g*, 37.0), Bi_2 (*g*, 31.8), BiO (*g*, 3.1)
HfC	1562	33 / 67	HfO_2 (*s*, 36.1), Bi_2 (*g*, 36.1), Bi (*g*, 24.0), CO (*g*, 2.5)
$HfSi_2$	-	-	-

Table 4d. Experimental Results – Zirconium and Hafnium Compounds, Bi_2O_3

(*a*) Mixture (*b*) wt% Ratio	Ignition	Self-Sustained Combustion	Amount Consumed	(*a*) Type (*b*) Duration (s)	Flame	(*a*) Sparks (*b*) Smoke (*c*) Slag
(*a*) ZrB_2 / Bi_2O_3 (*b*) 13 / 87	yes	yes	all	(*a*) flame (*b*) 0.6	moderate, orange	(*a*) some, orange (*b*) lots, yellow (*c*) some
(*a*) ZrC / Bi_2O_3 (*b*) 21 / 79	yes	yes	all	(*a*) spark/slag shower (*b*) 0.7	minimal, orange	(*a*) lots, orange (*b*) moderate, yellow (*c*) minimal
(*a*) ZrN / Bi_2O_3 (*b*) 26 / 74	yes	yes	all	(*a*) flame (*b*) 1.2	moderate, orange	(*a*) some, white (*b*) lots, yellow (*c*) some
(*a*) $ZrSi_2$ / Bi_2O_3 (*b*) 14 / 86	yes	yes	all	(*a*) incandescent slag pile (*b*) 5	minimal, orange	(*a*) none (*b*) some, yellow (*c*) large metallic beads
(*a*) HfB_2 / Bi_2O_3 (*b*) 20 / 80	yes	yes	all	(*a*) flame (*b*) 0.5	moderate, orange	(*a*) none (*b*) lots, yellow (*c*) small metallic beads
(*a*) HfC / Bi_2O_3 (*b*) 33 / 67	yes	yes	all	(*a*) burst (*b*) ~ 0.15	large, orange	(*a*) none (*b*) lots, yellow (*c*) none
(*a*) $HfSi_2$ / Bi_2O_3 (*b*) 20 / 80	yes	yes	all	(*a*) flame (*b*) 1	moderate, orange	(*a*) none (*b*) some, yellow (*c*) large metallic beads



Figures 1a-d. SEM images at 1,000 X.
TiB_2 (a) top left; ZrB_2 (b) top right; TiH_2 (c) bottom left; HfC (d) bottom right.

4. DISCUSSION

The fuel/oxidizer weight ratios estimated using the assumed reactions in Tables 2a-d are, for the most part, remarkably similar to those predicted with FactSage in Tables 3a-d. Exceptions include TiH_2/KNO_3 and reactions involving ZrC and HfC. Notably, the weight ratios predicted to give peak T_{ad} values (Tables 3a-d) either match those in Tables 2a-d or are seemingly fuel-rich. The greatest discrepancies are due to the predicted formation of $K_{(g)}$ and $CO_{(g)}$ instead of K_2O and CO_2. In other cases, the estimated and predicted weight ratios match or are similar despite substantially different predicted products such as potassium silicates and titanates. Potassium in the presence of boron is predicted to form KBO_2. Indeed, "KBO_2" is one known crystalline phase in the often glassy and non-stoichiometric $K_2O{\cdot}B_2O_3$ system [7,8].

Combustion temperatures of the metal-element compound/oxidizer mixtures are expected to be lower than those of the corresponding metal/oxidizer systems for two reasons. First, the metal-element compounds have negative enthalpies of formation. Second, production of additional reaction products in the liquid and gas phases (KBO_2, B_2O_3, SiO_2, and others) consumes energy that would otherwise increase temperature. As shown in Tables 5a and 5b, reactions involving the group 4 *metals* have greater predicted peak T_{ad} values (compare to Tables 3a-d). The combustion temperatures of metal/oxidizer systems, especially those containing very reducing metals and strong oxidizers, are limited by the substantial enthalpies of vaporization of the metal oxide products. The predicted adiabatic reaction temperatures and reaction products in Table 5a illustrate this well.

Table 5a. FactSage Calculations – Group 4 Metals, KNO_3

Reactant Fuel	T_{ad} (°C)	Fuel / KNO_3 (wt% ratio)	Major Products (*phase*, wt%)
Ti	3257	49 / 51	Ti_2O_3 (*l*, 58.5), K (*g*, 19.7), TiO (*g*, 8.8), N_2 (*g*, 7.0), TiO_2 (*g*, 5.5)
Zr	3717	58 / 42	ZrO_2 (*l*, 58.5), K (*g*, 16.2), ZrO (*g*, 9.3), ZrO_2 (*g*, 9.2), N_2 (*g*, 5.7)
Hf	4404	72 / 28	HfO_2 (*l*, 82.6), K (*g*, 10.8), N_2 (*g*, 3.8)

Table 5b. FactSage Calculations – Group 4 Metals, Bi_2O_3

Reactant Fuel	T_{ad} (°C)	Fuel / Bi_2O_3 (wt% ratio)	Major Products (*phase*, wt%)
Ti	2515	15 / 85	Ti_3O_5 (*s*, 17.2), TiO_2 (*l*, 5.9), Bi (*g*, 73.5), Bi_2 (*g*, 2.5)
Zr	3004	23 / 77	ZrO_2 (*l*, 30.0), Bi (*g*, 68.5)
Hf	3015	37 / 63	HfO_2 (*l*, 42.7), Bi (*g*, 56.0)

Figures 2a-d. Images from tests involving TiH_2 and HfC (see Tables 4a-d).
TiH_2/KNO_3 (a) top left; TiH_2/Bi_2O_3 (b) top right; HfC/KNO_3 (c) bottom left; HfC/Bi_2O_3 (d) bottom right.

Diverse reactivity was observed in qualitative ignition tests (Tables 4a-d). The titanium and zirconium disilicides were relatively unreactive, while the hafnium analogue and Ti_5Si_3 were much more reactive. Other compounds appeared to be more reactive with one of the oxidizers but less so with the other (examples include TiB_2, TiC, TiN, TiP, and ZrB_2). Of these, TiC and TiN were the least reactive. ZrC, ZrN, and HfB_2 were vigorously reactive with both KNO_3 and Bi_2O_3. The only two compounds that were violently reactive with both oxidizers were TiH_2 and HfC (Figures 2a-d). The HfC sample was composed of very fine particles and appeared to have a large surface area (Figures 1d and 3). Titanium hydride (TiH_2) and subhydrides (TiH_x) paired with $KClO_4$ have been studied

extensively as spark-insensitive pyrotechnic actuators and igniters intended for nuclear weapons applications [9]. *To the best of our knowledge, HfC has not been examined in a pyrotechnic context before.*

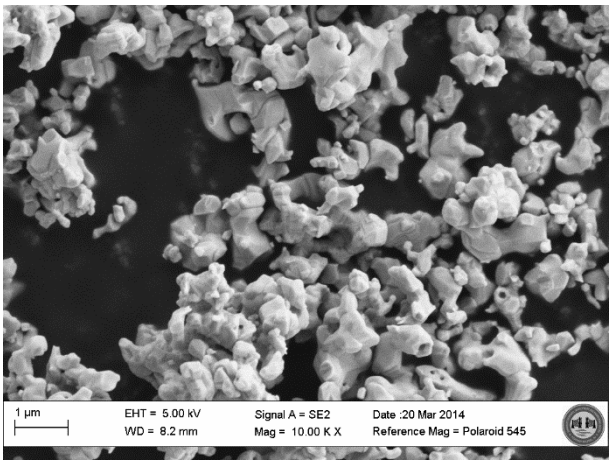


Figure 3. SEM image of HfC at 10,000 X.

The perceived vigorousness of the reactions is largely influenced by burning rate, temperature, and gas production. Compositions that burn rapidly at a high temperature with sufficient gas production produce a blinding flash, as observed for some of the fuel/KNO_3 mixtures. In contrast, the fuel/Bi_2O_3 mixtures seem to burn at lower temperatures, with even the most rapid reactions producing large orange fireballs of moderate intensity. These observations are in agreement with the corresponding trend in predicted T_{ad} (Tables 3a-d). Although, it should be noted that the predicted adiabatic reaction temperatures represent upper limits. The actual events are expected to occur at lower temperatures due to heat loss to the surroundings and the formation of non-equilibrium products.

Many of the compositions produced sparks, particularly the ones containing KNO_3 (Figure 4). Other notable qualitative characteristics included the violet and green hues of some of the flames, presumably caused by gaseous K and BO_2, respectively (Figures 2a, 2c, and 5). Some of the reactions with Bi_2O_3 produced metallic beads – elemental bismuth. Additionally, many of the reactions with Bi_2O_3 produced yellow smoke. This is attributed to the formation of gaseous Bi, which re-oxidizes in the air forming a yellow bismuth oxide aerosol.

Figure 4. $HfSi_2/KNO_3$ sparking (see Table 4b).

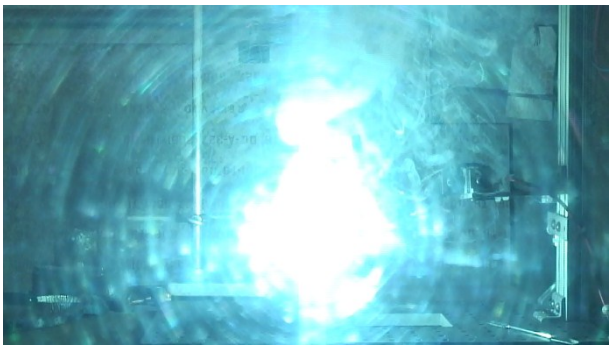


Figure 5. ZrB_2/KNO_3 green flame (see Table 4b).

5. SUMMARY AND CONCLUSIONS

Metal-element compounds of titanium, zirconium, and hafnium have been surveyed as pyrotechnic fuels. A variety of observed qualitative effects indicate that these fuels may be useful for multiple pyrotechnic applications. Considering that this survey made use of as-received materials, it may be possible to achieve more vigorous reactivity through the use of finer samples. Experiments with other oxidizers and characterization of mixture sensitivity to various ignition stimuli are areas of ongoing research in our laboratories.

6. ABBREVIATIONS AND ACRONYMS

AEE, Atlantic Equipment Engineers

ARDEC, Armament Research, Development and Engineering Center

RDECOM, Research, Development and Engineering Command

SEM, scanning electron microscopy

XRD, X-ray diffraction

XRF, X-ray fluorescence

7. ACKNOWLEDGMENTS

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